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Report No. 6

Quarterly Progress Report No. 11 | *September 1 to November 30, 1962*

SOLID PROPELLANT MECHANICAL PROPERTIES INVESTIGATIONS

Prepared for:

ROCKET RESEARCH LABORATORIES
AIR FORCE SYSTEMS COMMAND
EDWARDS, CALIFORNIA

CONTRACT NO. AF 04(611)-8388

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

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December 13, 1962

Report No. 6

Quarterly Progress Report No. II | *September 1 to November 30, 1962*

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By: *Norman Fishman* *James A. Rinde*

SRI Project No. PRU-4142

Approved:

Thor L. Smith

THOR L. SMITH, DIRECTOR
PROPULSION SCIENCES DIVISION

Copy No. 16

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I INTRODUCTION

An understanding of the mechanical behavior of solid propellants is required to advance the state-of-the-art of solid rocket technology. Current efforts in stress analysis of solid rocket grains, as well as in grain design, will be benefitted by additional knowledge of propellant failure mechanisms and by the establishment of failure criteria.

In past studies at Stanford Research Institute, we interrelated, over a restricted range of test conditions, the mechanical response and ultimate properties of propellants determined by different types of tests. Relatively good correlations between small deformation behavior and ultimate properties were obtained from uniaxial tension tests made under conditions of constant strain rate, constant load, and constant strain.

In the current research program we are investigating this area in more detail, with particular emphasis on the contribution made by the binder-oxidant interfacial region to the mechanical behavior of solid propellants. The general objective is to relate response and failure mechanisms to propellant microstructure.

This is the second Quarterly Progress Report of our investigations and covers the period September 1 to November 30, 1962.

II SUMMARY

Carboxy-terminated polybutadiene and polyurethane compositions for use in this program have been prepared; sufficient quantities of bagged and unbagged end-bonded specimens are in desiccated storage. Instron quality-control test data for all batches of the polyurethane composition are tabulated; although these data do not provide good evidence for batch-to-batch reproducibility, volumetric swelling ratios show little difference among batches of each composition.

The dilatometer has been completed and is undergoing final evaluation and calibration. Preliminary measurements of volume change during extension at constant strain rate demonstrate adequate sensitivity and effective operation.

Tests of desiccated end-bonded specimens at several constant strain rates and temperatures using the Instron have been completed; ultimate property data on carboxy-terminated polybutadiene composition AFBA-1 are not particularly consistent and do not yield a well-defined failure envelope, except in the case of batch NF2/238. Constant load and constant loading rate tests of the carboxy-terminated polybutadiene composition are being made and some preliminary data are presented.

III EXPERIMENTAL PROGRAM

A. Materials and Specimen Preparation

For the present program, four batches each of a carboxy-terminated polybutadiene (AFBA-1) and a polyurethane (AEBA-15) composition have been prepared. Quality control data for the four batches of AEBA-15 are presented in Table I. (Similar data for AFBA-1 were given in Quarterly Progress Report No. I.)

Table I

QUALITY CONTROL DATA FOR POLYURETHANE PROPELLANT (AEBA-15)

Batch No.	Test Temp. °F	σ_m psi	ϵ_m in./in.	σ_b psi	ϵ_b in./in.
NF 9/245	75	231	1.10	212	1.28
NF 10/246	75	219	0.874	202	1.012
NF 11/247	75	230	0.775	210	0.901
NF 12/248	75	209	0.778	200	0.827
NF 9/245	160	128	0.980	125	1.06
NF 10/246	160	135	0.721	127	0.804
NF 11/247	160	151	0.555	142	0.632
NF 12/248	160	126	0.632	117	0.663

Note: Results are the average of three tests. Tests were made at 2 in./min on JANAF specimens which had not been desiccated.

One means for determining similarities among batches is to compare volumetric swelling ratios of samples from each batch. This was done using chloroform as the swelling solvent and allowing 72 hours for equilibration. Results are shown in Table II.

Table II

VOLUMETRIC SWELLING RATIOS OF PROPELLANT BATCHES

Carboxy-Terminated Polybutadiene AFBA-1		Polyurethane AEBA-15	
Batch No.	q_m	Batch No.	q_m
NF 1/237	10.577 ± 0.169	NF 9/245	7.709 ± 0.004
NF 2/238	11.121 ± 0.066	NF 10/246	7.877 ± 0.094
NF 3/239	10.666 ± 0.032	NF 11/247	7.675 ± 0.002
NF 4/240	10.067 ± 0.145	NF 12/248	7.589 ± 0.152

Note: q_m values are averages of duplicate determinations, calculated as the ratios of swollen to dried volumes.

The data of Table II show that the crosslink densities of the four batches of AEBA-15 are very similar; crosslink densities of the batches of AFBA-1 are fairly close to each other, NF 2/238 having slightly lower and NF 4/240 having slightly higher values than the average. These data indicate that the batch-to-batch reproducibility of binder in each of these compositions was good. Referring to the Instron test results of Table I, and the quality control data for AFBA-1 shown in Quarterly Progress Report No. I, values of stress at maximum and at rupture show close similarity among batches, but corresponding values of elongation appear to vary excessively. However, greater variation is to be expected in ultimate property data, particularly elongation, then in small deformation data.

The results indicate that though the binder for each of several batches of a propellant is quite similar chemically, the similarity may not extend to the measured ultimate properties. Values of creep compliance for AFBA-1, shown later in this report, are evidence of fairly good batch-to-batch reproducibility. As additional mechanical property data are obtained, further consideration will be given to reproducibility of batches.

End-bonded specimens have been prepared from each of the batches of AFBA-1 and AEBA-15; some specimens were bagged with desiccant for use in the Instron and in the creep tester and others were prepared without bags for use in the dilatometer. Figure 1a is a photograph of a single bagged specimen with end tabs and a package containing four envelopes of six bagged specimens each, with desiccant in each successive enclosure. Figure 1b shows three specimens undergoing constant load tests; the specimen at the right has just ruptured at a point about 1/4 inch from the tab.

Prior to preparation of all the specimens, constant strain rate tests on similarly prepared specimens from a sample of TPH 1001 resulted in rupture at the tab. Thus, specimens of AFBA-1 were prepared by milling 0.03 inch of material from two opposite faces of the specimen, providing a test section nominal area of 0.44 x 0.50 inch. However, from extensive constant strain rate and constant load tests of this composition we found that rupture still occurred near the tab end. We therefore undertook a study of the effect of varying the cross sectional area of the test section on rupture behavior.

Duplicate specimens of AEBA-15, batch No. NF 9/245, were prepared with nominal cross sections of 0.32 x 0.50 inch, 0.38 x 0.50 inch, and 0.44 x 0.50 inch. The specimens were tested in the Instron at 75°F and at 1.2 in./min; results are shown in Fig. 2 as σ_m, σ_b, ϵ_m, and ϵ_b versus nominal cross sectional area. All specimens ruptured in the test section except those having the largest cross sectional area, which, as previously noted, broke near the tab end. The results indicate that (1) rupture properties are not particularly affected by the location of the point of rupture, provided it is not in the adhesive bond, and (2) there is a pronounced effect of cross sectional area on ultimate properties. Thus, subsequent specimens of AEBA-15 were prepared having a cross sectional area of 0.40 x 0.50 inch; however, rupture properties obtained on specimens of AFBA-1 whose dimensions are 0.44 x 0.50 inch are considered to be valid. The second finding above will be further investigated as time permits.

In addition to the results discussed above, measurements of effective gage length were made during the tests described. The method for determining L_e involved periodic photographing of the specimen having bench marks imprinted along the gage section. Photographic data were analyzed to determine actual strain rate and to verify strain rate uniformity along the gage section. Comparisons of actual strain rates and crosshead rates yield values of effective gage length. Results of these measurements are shown in Table III. Except for the last value, which is probably in error, the data of Table III show little effect on effective gage length from the reduction of test section cross sectional area for these specimens, and that the specimen length can be used as the gage length.

Table III

EFFECTIVE GAGE LENGTH RESULTS

(NF 9/245; Instron Tests at 75°F and 1.2 in./min)

Nominal Cross Sectional Dimensions (inch)	L_e (inch)
0.44 x 0.50	2.98
0.44 x 0.50	2.94
0.38 x 0.50	2.97
0.38 x 0.50	2.92
0.32 x 0.50	2.87
0.32 x 0.50	(3.28)

Considerable difficulty has been experienced with the successful employment of end-bonded specimens. Particularly at low temperatures, specimens have a tendency to rupture in the Rubbapox bond and at the Lucite-Lucite bond within the tab. These difficulties are most pronounced during Instron tests and are experienced only at the highest loads during creep tests. Improvements were made in the technique for bonding Lucite to Lucite and this problem has been largely eliminated.

However, rupture of the Rubbapox cohesive bond still occurs at low temperature and remains a problem in the Instron studies. The most serious difficulty arose during the preparation of specimens from batch NF 10/246, NF 11/247, and NF 12/248 of AEBA-15. Failure at the Rubbapox-Lucite interface at stress levels in the range 120 to 150 psi at 75°F resulted in failure to obtain constant strain rate data for desiccated specimens from these batches of propellant. (Later tests of specimens equilibrated at ambient humidity were conducted successfully.) We believe, however, that we can use the specimens for the major part of the projected constant load work. Thus, the primary studies of the behavior of AEBA-15 will of necessity be undertaken with specimens from batch no. NF 9/245, and if required, additional specimens will be prepared of the remaining material from these batches.

There are several possible causes for the bonding difficulties. Bonding a large sheet of Lucite to a block of propellant may result in inadequate moisture for the Rubbapox cure, though in most cases, the cure appeared to be normal. The latest difficulty of adhesion to the Lucite was probably due to improper preparation of the Lucite surface. It is also possible that desiccation serves to weaken the Rubbapox. Future work with specimens equilibrated at prescribed levels of humidity will serve to verify or refute this latter possiblity. In any event, we plan to continue our work with the specimens already prepared; prior to making additional specimens, we will reconsider the relative advisability of bonding large blocks or preparing individual specimens.

B. Apparatus

The dilatometer has been fabricated and assembled; final check out of components and instrumentation is in progress. The effectiveness of the temperature control system is being determined by measurement of temperatures at various locations in the dilatometer body for different control settings in the constant temperature bath. Force and pressure transducers and associated instrumentation have been calibrated. The strain-measuring potentiometer and constant load servo system have not yet been evaluated and calibrated. Miscellaneous features such as the limit switches and revolution indicator will be completed.

Figures 3a and 3b are two views of the assembly. The output shaft of the Servo-Tek drive is geared to the gear reduction system which provides for a wide selection of constant strain rates. The output shaft of the gear train then enters the magnetic coupling-brake assembly. Next in line are the sprocket and chain for constant load assist, followed by the bevel gear which is coupled to the constant load servo motor and to the strain potentiometer. During constant load tests the Servo-Tek drive and gear train are inactive. The drive shaft enters the test cavity of the dilatometer through a Del Manufacturing Company shaft seal. The force transducer is placed at the top of the test cavity external to the dilatometer; the differential pressure transducer, mounted behind the flexible drive shaft coupling, senses pressure near the tops of the test and comparison cavities.

A preliminary run was made under constant strain rate conditions. The chart speed for the force record was too slow; consequently, stress-time data were extracted from a very short record. However, the pressure-time data were smooth and demonstrated good operation of the volume change measuring system. The values of volume change may not be accurate due to the possibility of low rate leakage during the test. Figure 4 shows the data from this preliminary run plotted as log volume and log stress versus log (λ). Values of ν, Poisson's ratio, were calculated from these data; at strains up to 0.07, ν was found to be greater than 0.495, and at a strain of about 0.35, the value for ν was 0.31.

C. Results

1. Constant Strain Rate

Extensive tests of the carboxy-terminated polybutadiene formulation AFBA-1 have been carried out using the Instron tester. These included strain rates from 4 to 0.004 min^{-1} and eight temperatures from 160° to -50°F. The results of tests on batch NF 2/238 are shown in Figs. 5 and 6, presented as failure envelopes of $\sigma_m - \epsilon_m$ and $\sigma_b - \epsilon_b$ data, respectively. Figure 7 shows a comparison of constant load rupture data with the constant strain rate failure envelopes.

The constant strain rate data were generally scattered, the best definition of the failure envelopes resulting from tests of batch NF 2/238. Small differences in moisture content at near dryness, where moisture is known to have a large effect on mechanical properties, is a possible reason for the wide variability of data. Another reason is rupture of the specimen at the Rubbapox bond, especially at the lower temperatures, which invalidates or brings into question many of the tests.

Two points of interest arise from these data; first, the range of ultimate strain covered by the failure envelope is fairly small and secondly, the constant load data agree very well with the constant strain rate data.

Constant strain rate tests on the polyurethane composition AEBA-15, batch NF 9/245 have been completed; however, no analysis of the data has yet been made. Further constant strain rate work and data analysis will be undertaken as additional information becomes available from other parts of the program.

2. Constant Load

Tests conducted under conditions of constant load during this past quarter included 9 loads at 100°F and 4 loads at 40°F on composition AFBA-1, batch NF 2/238, and 2 loads at 100°F on batches NF 1/237, NF 3/239, and NF 4/240 of the same propellant. No tests have yet been made on the polyurethane propellant AEBA-15.

The experimental data from constant load tests on batch NF 2/238 at 40° and 100°F are shown as log-log plots of compliance versus time in Figs. 8 and 9. Similarly, a comparison of batches NF 1, NF 2, NF 3, and NF 4 under conditions of constant load is shown in Fig. 10 for two different load levels. In both cases it is seen that rupture occurs at a lower strain and shorter time for the specimens of batch NF 2/238. This may be due to the differences among batches of propellant as shown by the swelling ratios, Table II.

In contrast to the results of constant strain rate tests on all batches of the AFBA-1 composition, the tests at constant load have yielded data which show good batch-to-batch and within-batch consistency. Difficulties encountered in the constant strain rate tests due to rupture in the Rubbapox bond have not occurred in tests at constant load. However, the effect of possible humidity variations is not known and may cause small differences in the strain at break or in the compliance in the constant load tests.

In general, the results of this work on desiccated specimens have shown that rupture occurs in the linear portion of the logarithmic strain-time curve. Previous tests on samples at near ambient humidity ruptured at some point in a "third-region" of behavior where the rate of strain increase is greater than in the linear region. This region of "catastrophic dewetting" seems to be absent in tests on dry specimens.

3. Constant Loading Rate

Limited constant loading rate tests on NF 2 at 100°F were carried out at five different loading rates. The results are presented in Figs. 11 and 12; the data are consistent and useful correlations should be obtainable when more tests have been completed.

IV FUTURE WORK

Final calibration and check-out of the dilatometer will be completed and experimentation will begin in the near future. Initial work will consist of tests at constant strain rate and constant load at 100°F. Analyses of data and interpretation of volume change results will be undertaken as sufficient quantities of data become available. Methods for data analysis will be devised to enable separation of the time-dependence of the binder elongation and binder-oxidant separation processes.

ACKNOWLEDGMENTS

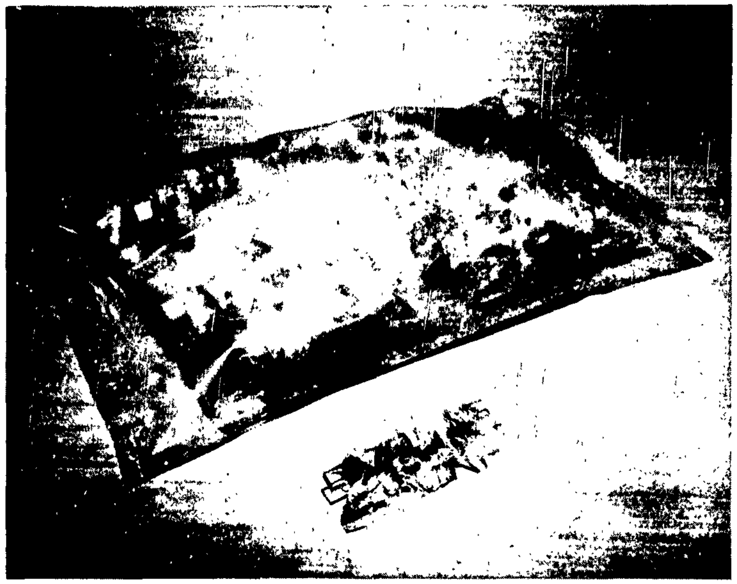
The authors are grateful for the suggestions of Dr. Thor L. Smith and for the contributions of Leon Hiam and Edward A. Hillam. The program is benefited by the close cooperation with the cognizant staff of the Rocket Research Laboratories, Edwards Air Force Base.

Norman Fishman

Norman Fishman, Manager
Propellant Evaluation Section

James A. Rinde

James A. Rinde
Chemist



a

b

FIG. 1 PHOTOGRAPHS OF BAGGED SPECIMENS

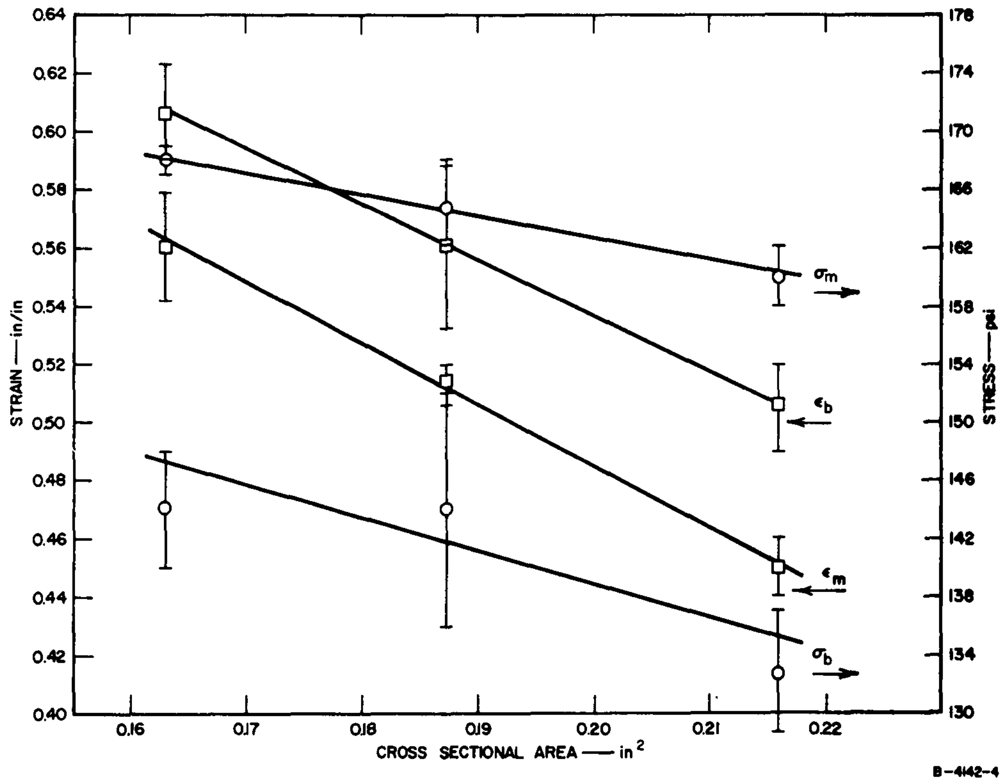
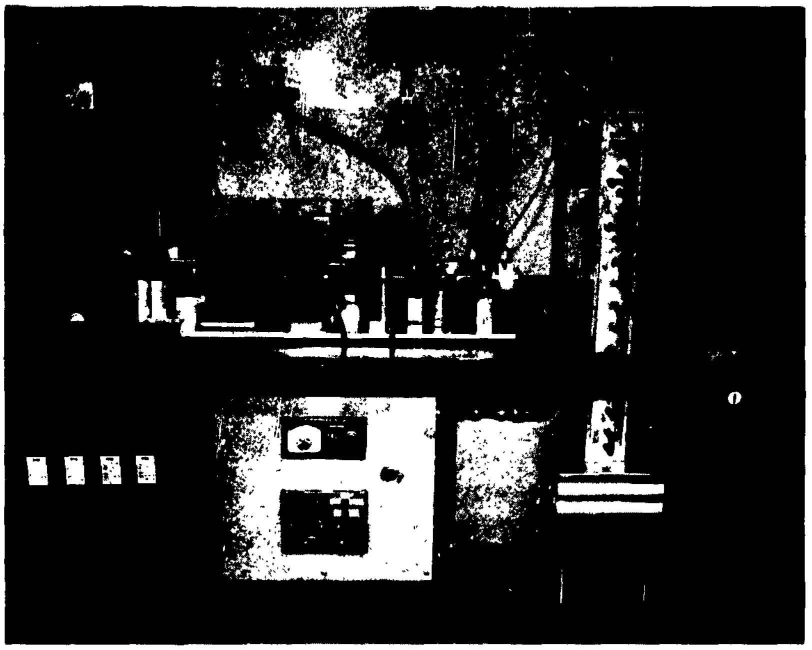
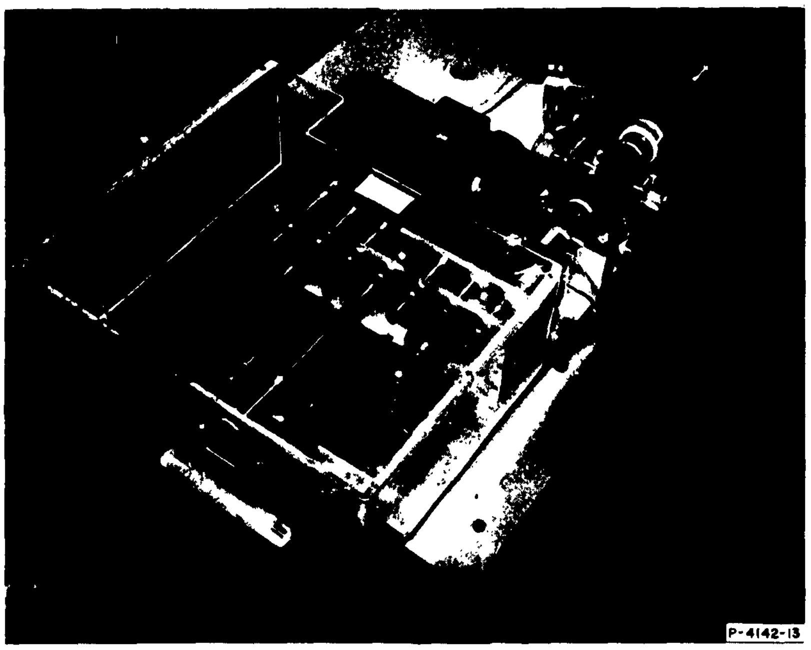


FIG. 2 ULTIMATE PROPERTIES AS A FUNCTION OF SPECIMEN CROSS SECTIONAL AREA (Desiccated Specimens of Polyurethane Composition AEBA-15)



a



b

FIG. 3 PHOTOGRAPHIC VIEWS OF THE DILATOMETER

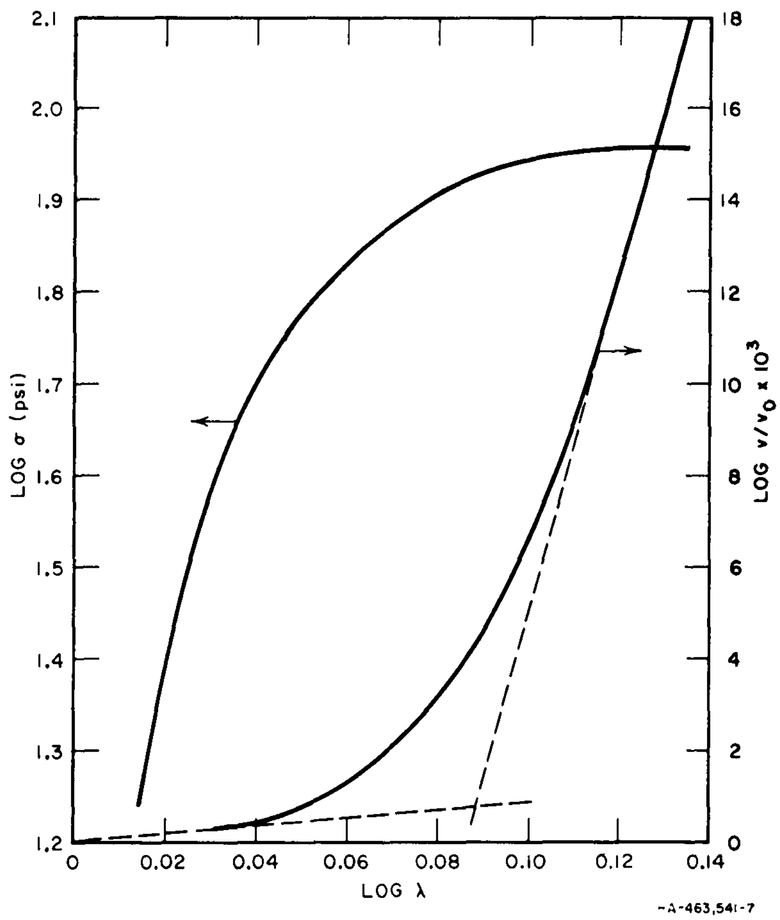


FIG. 4 TYPICAL CURVE FOR VOLUME vs. λ AT CONSTANT STRAIN RATE
(Carboxy-terminated Polybutadiene Composition AFBA-1)

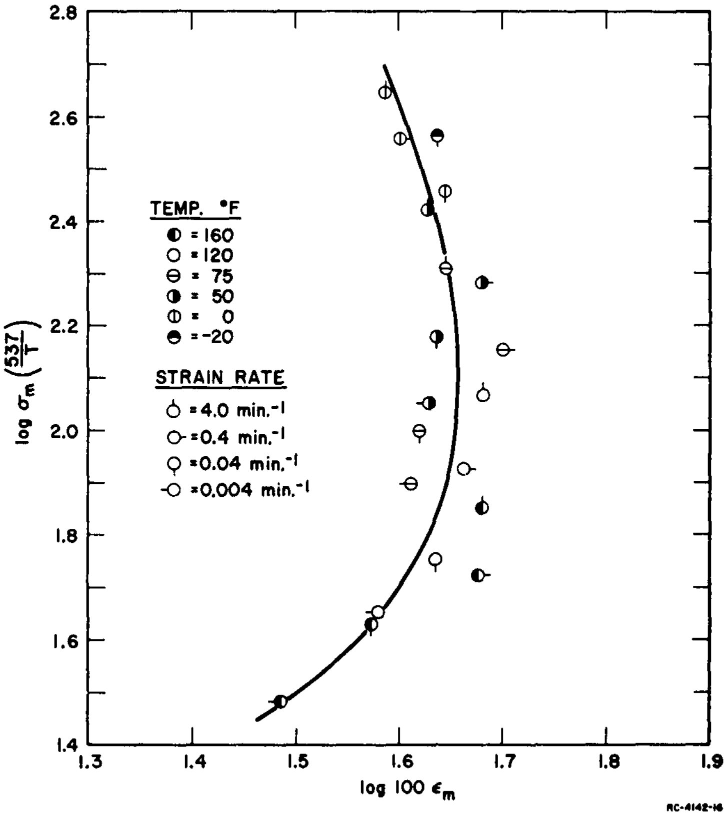


FIG. 5 FAILURE ENVELOPE ($\sigma_m - \epsilon_m$) FOR AFBA-1, BATCH NO. NF2/238

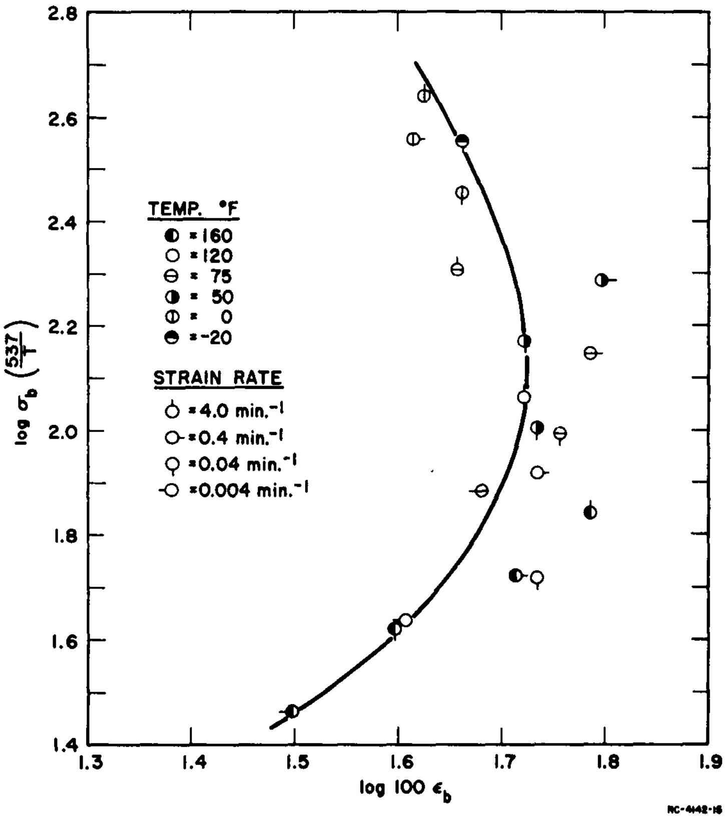


FIG. 6 FAILURE ENVELOPE ($\sigma_b - \epsilon_b$) FOR AFBA-1, BATCH NO. NF2/238

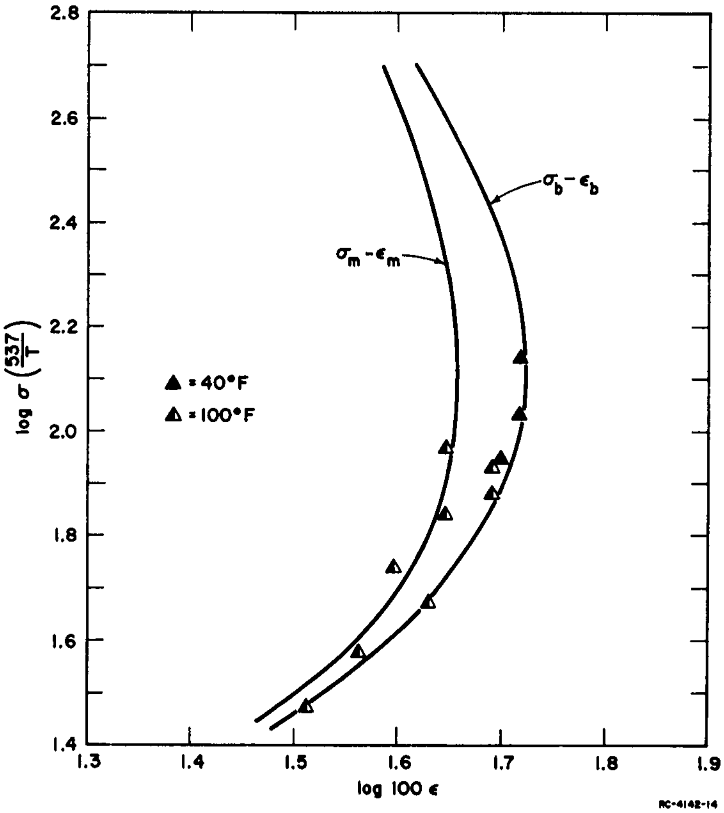


FIG. 7 COMPARISON OF CONSTANT LOAD RUPTURE WITH FAILURE ENVELOPES FOR AFBA-1, BATCH NO. NF2/238

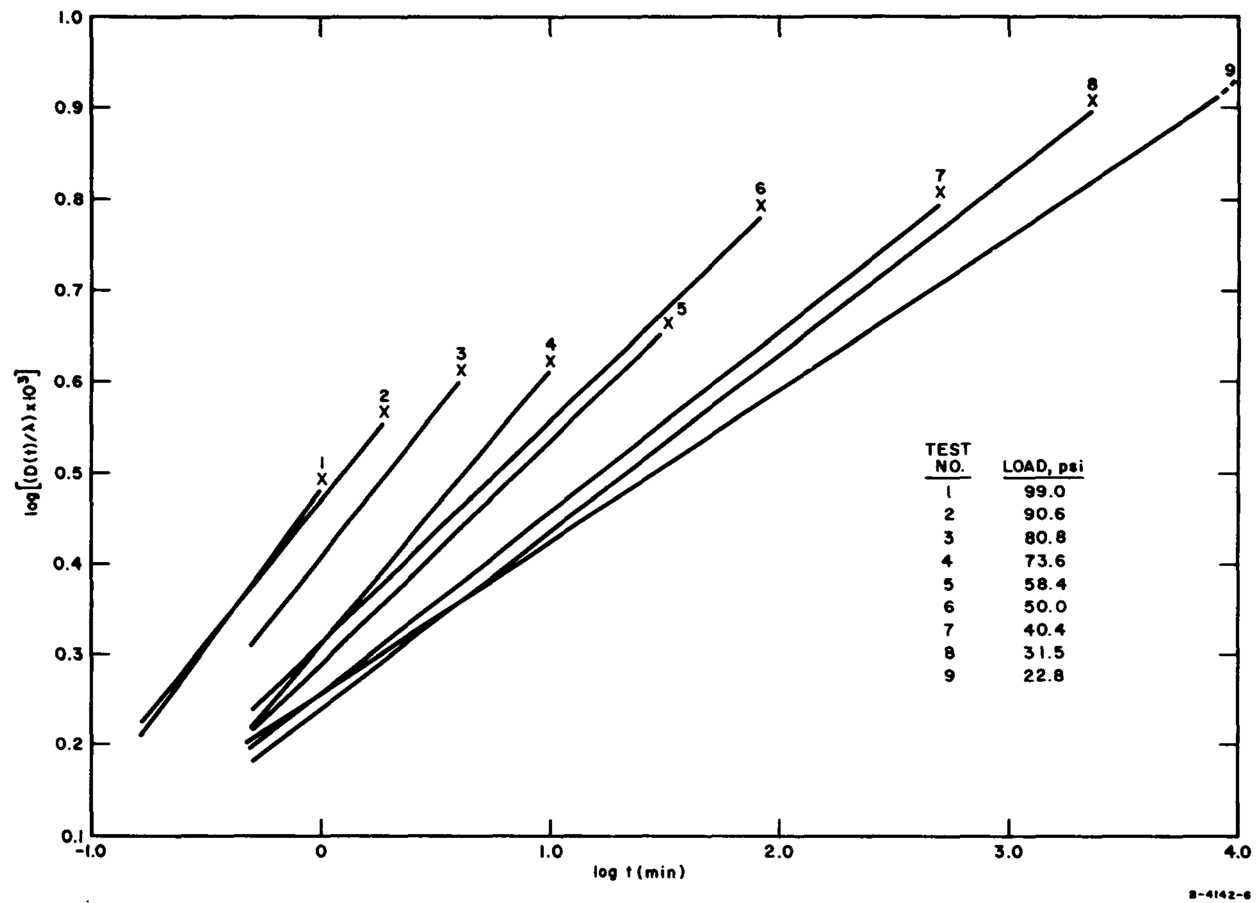


FIG. 8 CONSTANT LOAD RESULTS FOR AFBA-1, BATCH NO. NF2/238 TESTED AT 100°F

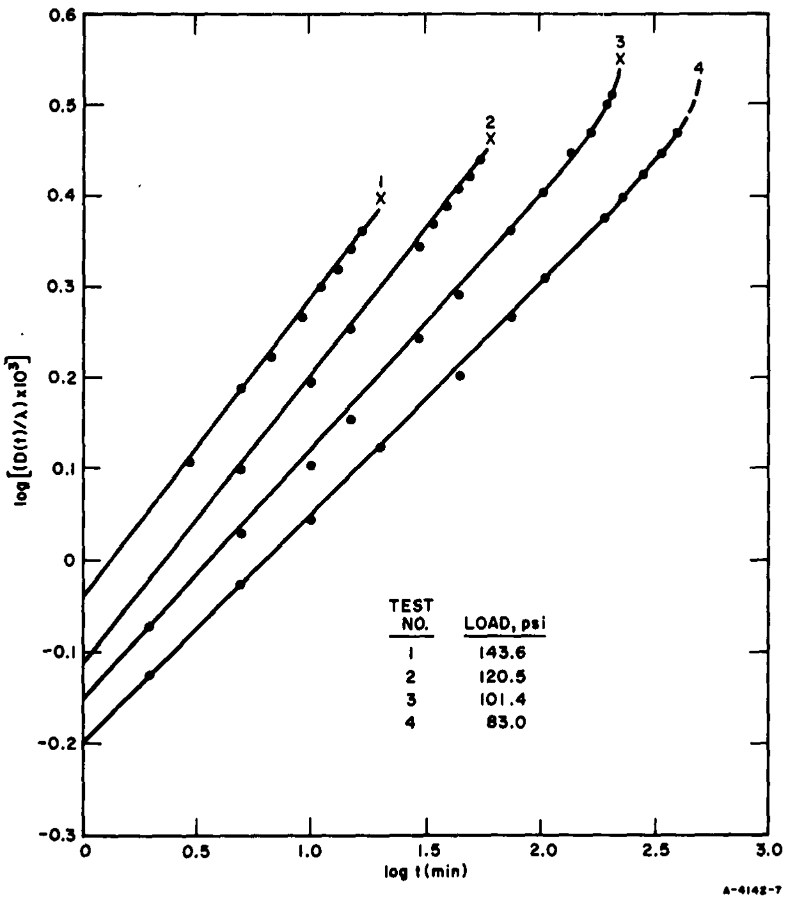


FIG. 9 CONSTANT LOAD RESULTS FOR AFBA-1, BATCH NO. NF2/238 TESTED AT 40°F

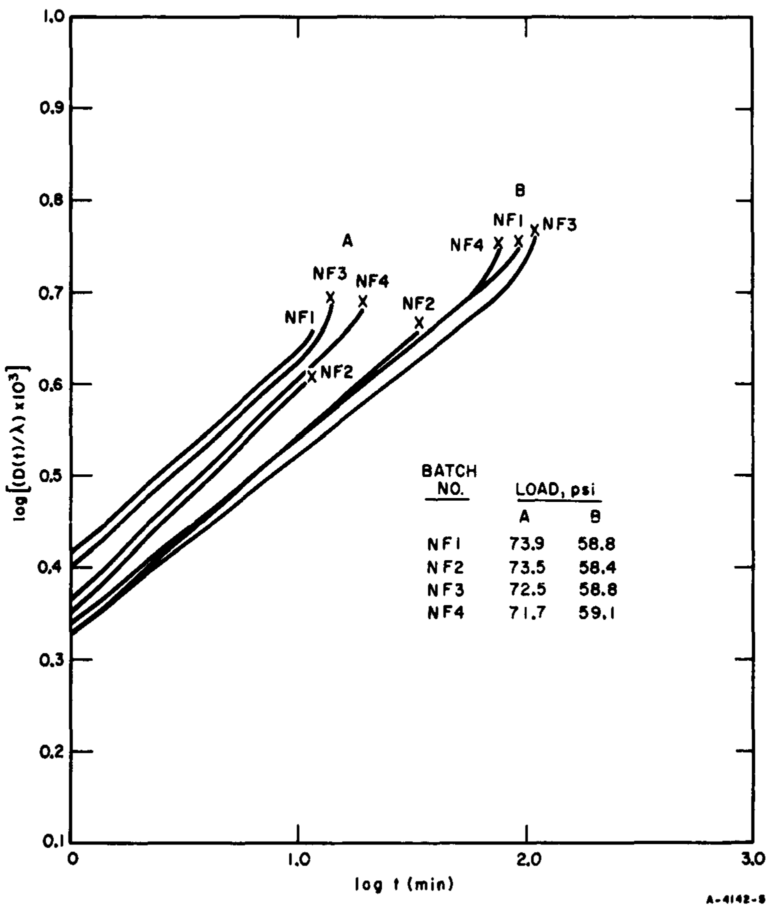


FIG. 10 CONSTANT LOAD RESULTS FOR FOUR BATCHES OF AFBA-1

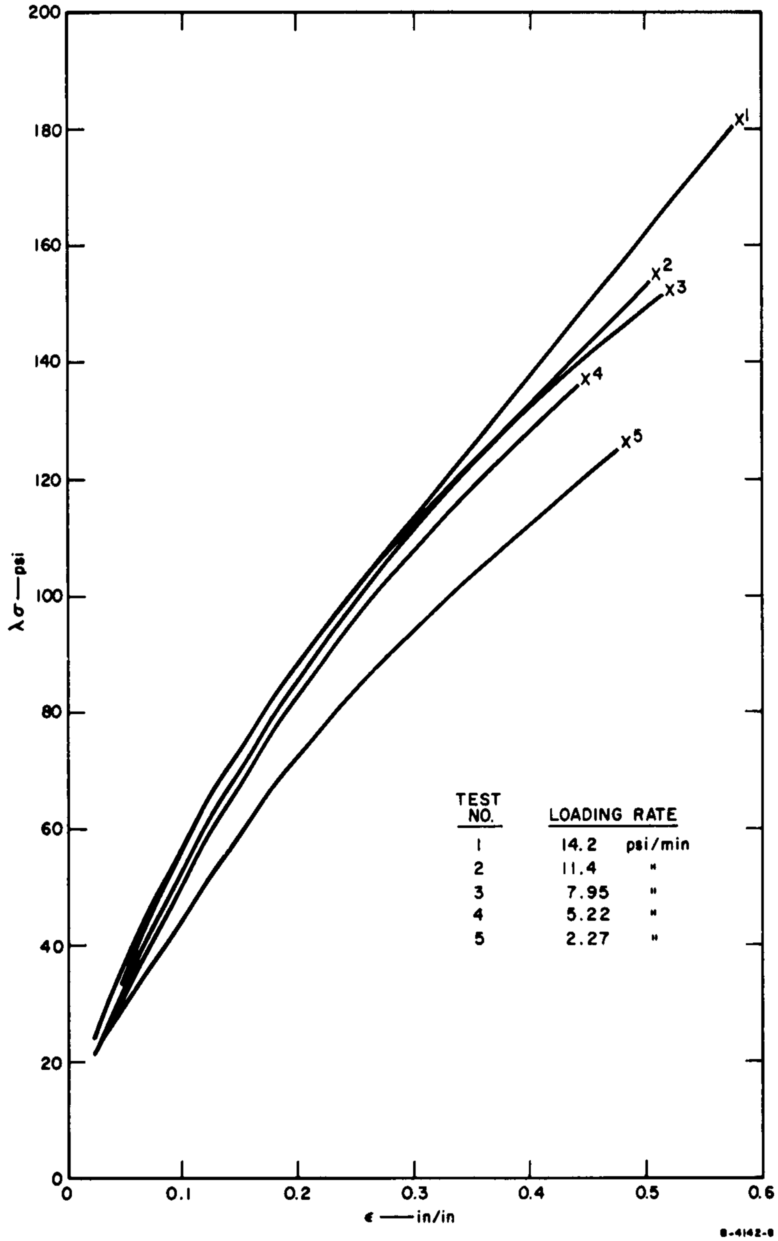


FIG. 11 STRESS-STRAIN RELATIONSHIPS FOR AFBA-1 TESTED AT CONSTANT LOADING RATE, 100°F

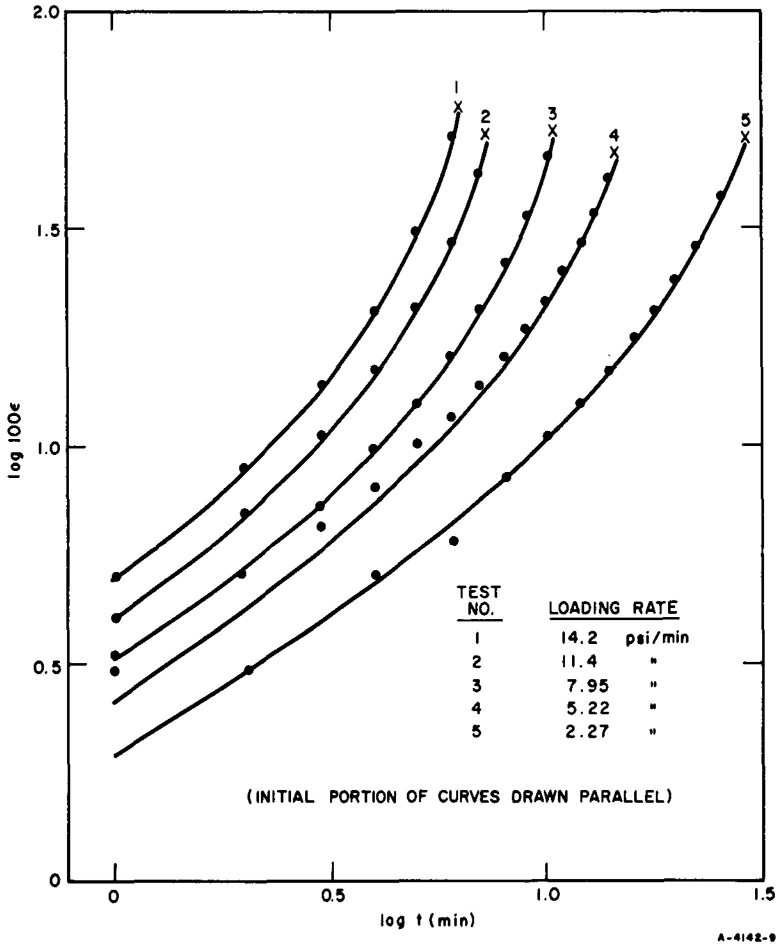


FIG. 12 STRAIN-TIME RELATIONSHIPS FOR AFBA-1 TESTED AT CONSTANT LOADING RATE, 100°F

STANFORD
RESEARCH
INSTITUTE

MENLO PARK
CALIFORNIA

Regional Offices and Laboratories

Southern California Laboratories
820 Mission Street
South Pasadena, California

Washington Office
808 17th Street, N.W.
Washington 5, D.C.

New York Office
270 Park Avenue, Room 1770
New York 17, New York

Detroit Office
The Stevens Building
1025 East Maple Road
Birmingham, Michigan

European Office
Pelikanstrasse 37
Zurich 1, Switzerland

Japan Office
911 Iino Building
22, 2-chome, Uchisaiwai-cho, Chiyoda-ku
Tokyo, Japan

Representatives

Honolulu, Hawaii
Finance Factors Building
195 South King Street
Honolulu, Hawaii

London, England
19 Upper Brook Street
London, W. 1, England

Milan, Italy
Via Macedonio Melloni 40
Milano, Italy

London, Ontario, Canada
P.O. Box 782
London, Ontario, Canada